Recoverable high energy compounds by reacting methane and nitrogen under high pressure

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The search for the stable polymeric forms of solid nitrogen is of great importance in view of its potential application as a high-energy-density material. Using first principles calculations combined with an effective crystal structure search method, we demonstrate that nitrogen can react with methane under relatively moderate pressures. The structures and the stability strongly depend on the composition. CN_2H_4 and CN_4H_4 compounds become stable in *Pca*2$_1$ and *I*-42*d* phases under pressures of 11 and 41 GPa, respectively. Especially, CN_4H_4 is recoverable as a metastable high energy material at ambient condition, and can release enormous amount of energy (6.43 kJ·g^{-1}) while decomposing to molecular nitrogen and methane.

High-energy-density materials (HEDM) are of great importance in many areas, including energy storage, rocket propellants and explosives. Polynitrogen materials have been the promising HEDM candidates because of the large energy difference between the structures consisting of single bonds and triple bonds.[1] Since diatomic N_2 molecule is the most stable form adopting the strongest-known N≡N triple bond[2], a great amount of energy will be released when the polymeric nitrogen materials bonded with single bonds decompose to N_2. High pressure has been verified as an effective way to break the extremely strong triple N≡N bond and obtain polymeric nitrogen materials[3] with N-N bond.

Due to the difficulty of synthesizing polymeric nitrogen in experiment, the first principles computational study under high pressure, especially coupled with the automatic crystal structure search algorithms, has produced considerable success. Following the first-principles prediction of single-bonded covalent solids with three-coordinated nitrogen atoms proposed by McMahan and Lesar[4], many other theoretical predictions of monatomic structures were studied, such as the cubic gauche (cg)[5], black phosphorus, α-arsenic[6,7], *Cmcm* chain[8], N_2-N_6[8], cis-trans chain [9], layered boat[10], eight-member rings[11], poly-N[12], layered *Pba*$_2$ (LP)[13], helical tunnel *P*2$_1$2$_1$2$_1$ structure[13,14] and cage-like diamonded nitrogen[15]. Experimentally, single-bonded framework of cg structure has been synthesized successfully at high pressure (110 GPa) and high temperature (2000 K) [3,16]. Most recently, the layered *Pba*$_2$ structure was observed[17]. However, both cg-N and LP-N are metastable at pressures above 42 GPa at room temperature[3]. Therefore, the strict experimental synthesis conditions and the absence of recovering to ambient conditions impede the usage of these single-bonded polymeric nitrogen as HEDM candidates.

In order to lower the synthesis pressure of single-bonded polymeric nitrogen, efforts have been directed toward searching novel polymeric nitrogen materials by introducing other elements into "precompressing" N_2. Moreover, many metal nitrides[18-24], and nonmetal nitrides[25-28] have also been studied. Recently, Raza et al. found that nitrogen can react with carbon monoxide at pressures above 52 GPa. Upon reducing the pressure to ambient, the corresponding compound maintains the three-dimensional covalent framework and is dynamically stable.[29] These studies show that the inclusion of hetero-atomic bonds, such as C-N and N-O etc., can help the formation of nitrogen rich polymeric materials. However, the poorly designed compositions and structures might greatly lower the energy densities of the nitrogen based HEDM[30].

Three factors are vital for obtaining high energy density in the nitrogen based HEDM: (i) large number of single bonded polymeric nitrogen; (ii) high nitrogen content, and (iii) large weight ratio (w.t.) of nitrogen[18,26]. Motivated by the activation of C-H bond[31] and light weight of methane, we proposed that methane can react with nitrogen and form stable covalent compounds under high pressures. Moreover, whether these compounds can be recovered at ambient pressure were examined. The infrared and ultraviolet absorption spectra of mixtures solid nitrogen and methane have been studied in order to characterize the lower atmosphere of Titan. Although the production of azide radicals was observed[32,33] in these studies, no reaction between the two or the formation of polymeric

compounds with covalent framework have been reported so far.

Methane is known to form longer hydrocarbon chains from theoretical and experimental studies of high-pressure structures[34]. Once N_2 reacts preferentially with the hydrocarbons, amines or diamines will be formed in the mixture of methane and nitrogen at high pressure. Note that amine and diamines, as typical compounds of ternary organic carbon nitrogen hydrides, have also been concerned for their wide utility of azo dyes, drugs, and abatement of greenhouse gases[35].

In this work, exploration of the reaction between nitrogen and methane was performed in a large pressure range from 0 to 50 GPa, using the swarm-structure searching algorithm in conjunction with first-principles calcuations.[36,37] Our study shows that nitrogen can react with methane at a fairly low pressure (8 GPa) and form high-energy-density compounds with various compositions and structures, including one-dimensional polymeric crystal such as CN_2H_4 and three-dimensional extended solid such as CN_4H_4. Among all the compounds, a three-dimensional solid CN_4H_4 (*I*-42*d*) shows a surprisingly high energy density of about 6.37 kJg^{-1} that is the highest among all the known polynitrogen compounds, making CN_4H_4 a promising candidate for nitrogen based HEDM.

Our structure searches are performed using the particle swarm optimization (PSO) method as implemented in CALYPSO code[36-38], which is specially designed for global structural minimization unbiased by any known structural information. The approach is based on a global minimization of free energy surfaces obtained from ab initio total-energy calculations. This method has been benchmarked on various known systems, ranging from elements to binary and ternary compounds[39-42]. Total energy calculations were performed in the framework of density functional theory within the Perdew-Burke-Ernzerhof[43] parameterization of generalized gradient approximation[44] as implemented in the VASP (Vienna Ab Initio simulation package) code[45]. The projector-augmented wave (PAW) method[46] was adopted with the PAW potentials taken from the VASP library where $2s^22p^2$, $2s^22p^3$ and $1s^1$ are treated as valence electrons for C, N and H atoms, respectively. The use of the plane-wave kinetic energy cutoff of 1000 eV and dense k-point sampling were shown to give excellent convergence of total energies. Phonon calculations were performed for all promising structures using the phonopy code[47]. The harmonic interatomic force constants are calculated by 2 × 2 × 2, 2 × 1 × 2, 1 × 2 × 2 and 2 × 2 × 2 supercells for *P*1-C_2NH_8, $P2_1$-CNH_4, $Pca2_1$-CN_2H_4 and *I*-42*d*-CN_4H_4, respectively.

It is important to recognize that the energetics might be largely changed by the inclusion of the large zero-point energy (ZPE) in light-element systems (elemental solids and their compounds). As a result, the ZPEs for *I*-42*d*-CN_4H_4, $P2_12_12_1$-CH_4 and $P4_12_12$-N at 20 GPa are calculated to be as large as 233, 275 and 108 meV/atom, respectively. Indeed, the contribution of ZPE to formational enthalpies is 57 meV/atom, which is typically big. Therefore, the ZPE was considered in the calculations of the formation enthalpies of CH_4-N_2 compounds. The ZPE calculations were performed using the quasi-harmonic approximation as implemented in the Phonopy code[47]. Generally, van der Waals (vdW) interactions in molecular crystals might be significant, and it affects the reaction enthalpies, especially considering different bonding nature of the product compounds. We therefore also include the vdW forces using the vdW density functional (vdW-DF2) in the calculations of the formation enthalpis and phonon spectrums of CH_4-N_2 compounds throughout the pressure range.

Thermodynamic stability of CH_4-N_2 system with various stoichiometries of $(CH_4)N_x$ (x = 0.25, 0.5 &1-6) were thoroughly examined by comparing the formation enthalpies[41] at pressures of 0, 5, 10, 20 and 50 GPa, relative to the dissociation into solid CH_4 and N_2, as shown by the convex hull (Fig. 1). The formation enthalpies of all stoichiometries are positive at 0 GPa, indicating there is no reaction between CH_4 and N_2 at ambient condition. This is consistent with the experimental observation that no stable CH_4-N_2 compounds can form at ambient pressure. Fig. 1 also shows that the thermodynamically stable stoichiometry varies with pressure. In the low-pressure range (< 10 GPa), C_2NH_8 is the most stable species, while CN_2H_4 is the most stable one in the high-pressure range (> 10 GPa). Besides, C_2NH_8, CNH_4, CN_2H_4 and CN_4H_4 are all stable at 50 GPa.

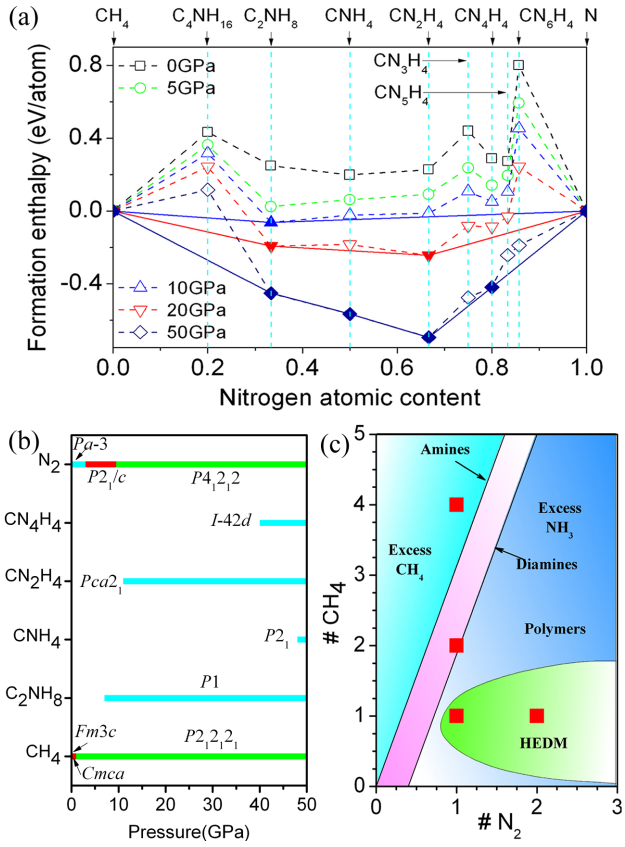

Figure 1 Phase stabilities of CH_4-N_2 compounds. (a) The enthalpies of formation for various CH_4-N_2 compounds under a series of pressures. The dotted lines connect the data points, and the solid lines denote the convex hull. The data show that C_2NH_8, CNH_4, CN_2H_4, and

CN_4H_4 are the stable stoichiometries, and CN_2H_4 is the most stable stoichiometry at high pressures. vdW interactions and ZPE corrections are considered during our calculations. (b) Predicted stable pressure ranges for CH_4-N_2 compounds, different colors present different phases in the corresponding stable pressure ranges. (c) Division of CH_4-N_2 phase diagram into regions of molecular compounds (amines, diamines), polymeric compounds, and the most interesting HEDM region. Red squares are our predicted stable structures.

The outcomes of reactions of methane and nitrogen are abundant and interesting. At methane-rich side, the outcomes are mainly amines or diamines, which have formula C_mNH_{2m+3} (e.g., C_2NH_8) with the framework of H_2N–$(CH_2)_{m-1}$–CH_3, or $C_mN_2H_{2m+4}$ (e.g., CNH_4) with the framework of H_2N–$(CH_2)_m$–NH_2, respectively. While, on the nitrogen-rich side, the outcomes are mainly carbon-nitrogen polymers (e.g., CN_4H_4 and CN_2H_4). The outcomes of CH_4-N_2 phase diagram are shown in Fig. 1c.

To ensure the dynamic stability of these four newly uncovered CH_4-N_2 compounds, we calculated their phonon dispersions (Supplemental Material Fig. S1)[48]. These four methane-nitrogen compounds, including C_2NH_8, CNH_4, CN_2H_4 and CN_4H_4, show no imaginary vibrational modes over the Brillouin zone at corresponding pressures (i.e. C_2NH_8 and CN_2H_4 at 20 GPa; CNH_4 and CN_4H_4 at 50 GPa), confirming they are dynamically stable under the pressure range of thermodynamic stability.

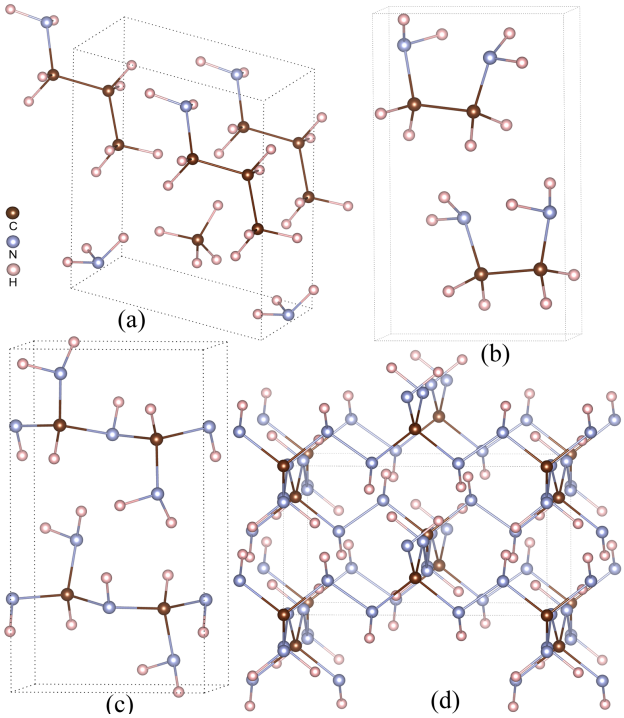

Figure 2 Crystal structures of CH_4-N_2 compounds. (a) *P*1 phase at 10 GPa for C_2NH_8. This phase can be seen as a mixture of molecular units: C_3NH_9 + NH_3 + CH_4. (b) $P2_1$ structure for CNH_4 at 50 GPa. This phase can be seen as a molecular phase with formula units $C_2N_2H_8$. (c) the polymeric $Pca2_1$ phase of CN_2H_4 at 20 GPa. (d) *I*-42*d* phase of CN_4H_4 at 50 GPa.

For C_2NH_8 compounds, we found a unique triclinic structure with *P*1 symmetry, as depicted in Fig. 2a. It is thermodynamically stable above pressure 8 GPa. This molecular phase of $(C_2NH_8)_2$ can be seen as a mixture of molecular units of C_3NH_9 + NH_3 + CH_4. To distinct the type of methane nitrides, *p*- prefix and *m*- prefix are used referring to a polymeric structure and a molecular structure, respectively. The coordination numbers of C and N for *m*-C_2NH_8 are 4 and 3, respectively, which can be confirmed by the calculated electron localization function (ELF)[49] (Fig. S2a)[48]. The nearest C–C and C–N distances in the unit of C_3NH_9 are 1.52 Å and 1.47 Å at 20 GPa, respectively, which are similar to the C-C single bond length (1.54 Å) of diamond and C-N single bond length (1.48 Å) of diamond-type C_3N_4 at ambient pressure. The bond angles of H–C–H/H–N–H and bond lengths of C–H/N–H in C_2NH_8 at 20 GPa are very similar to that of free CH_4/NH_3 molecules. The Bader charge analysis[50] reveals the C_3NH_9, NH_3, and CH_4 units are all neutral molecules in *m*-C_2NH_8.

As shown in Fig. 1, the predicted monoclinic structure of *m*-CNH_4 with $P2_1$ symmetry (Fig. 2b) can be stable above 48 GPa. This molecular phase consists of U-type H_2N–CH_2–CH_2–NH_2 molecules, can be seen as a typical diamine. Similar to *m*-C_2NH_8, the coordination numbers of C and N in CNH_4 are 4 and 3, respectively, which can be characterized via the bond length and ELF (Fig. S2b)[48]. The single bond lengths of C–N/C–C in *m*-CNH_4 at 20 GPa are similar to that of diamond at normal conditions. The bond lengths of C–H/N–H (1.06/1.02 Å) and bond angles of H–C–H/H–N–H (ranges: 106.81–107.05°/103.79–106.20°) in CNH_4 are almost same as that free CH_4 (1.07 Å, 109.28°), NH_3 (1.02 Å, 107.18°) and C_2H_6 (1.09 Å, 111.17°) molecules.

The predicted *p*-CN_2H_4 crystalized in monoclinic structure with $Pca2_1$ symmetry (Fig. 2c), which can be thermodynamically stable above 11 GPa (Fig. 1). In this phase, one-dimensional polymers are formed based on an infinite nonlinear …N–C–N–C… chains frameworks. The coordination numbers of C and N in this phase are 4 and 3, respectively, which can be verified by the calculated ELF (Fig. S2c)[48]. The bond lengths of N–H, C–H, C–N and bond angles of H–N–H are all similar to that of *m*-CNH_4 and *m*-C_2NH_8 at same pressure.

The predicted *p*-CN_4H_4 crystal is thermodynamically stable above 41 GPa. It crystalized in a tetragonal structure with *I*-42*d* symmetry, in which a three-dimensional framework is formed (Fig. 2d). The three-dimensional framework in *I*-42*d* phase consists of nonplanar three-coordinated nitrogen atoms and tetrahedral four-coordinated carbons, which are both saturated by H atoms.

Interestingly, as shown in Fig. 3b and S1d, phonon calculations of *I*-42*d* structure were performed in the pressure range from 0 to 50 GPa yield no imaginary vibrational modes, suggesting that it is dynamically stable. The result is significant, since it indicates that the three-dimensional framework *I*-42*d* phase of *p*-CN_4H_4 is mechanically stable and can be recovered to ambient pres-

sure. In contrast, the linear polymeric $Pca2_1$ structure of p-CN_2H_4 is only dynamically stable above approximately 10 GPa. At 10 GPa and below, it has negative frequencies corresponding to an antiparallel motion of the weakly bound polymer chains.

Fully covalent three-dimensional frameworks consisting of C–N and N–N of I-42d phase for p-CN_4H_4, can be verified via the observation of charge localization between the nearest-neighbor C–N and N–N atoms from the calculated ELF at 0 GPa (Fig. 3d). Furthermore, Crystalline Orbital Hamiltonian Population (COHP) and Integrated Crystalline Orbital Hamiltonian Population calculations (ICOHP)[51] were performed to confirm the C–N and N–N covalent bonding for I-42d phase of p-CN_4H_4 at 0 GPa. The results of COHP and ELF clearly reveal the covalent nature of the C-N and N-N bonds in this structure. The electronic band structures and density of states (DOS) of CN_4H_4 at 0 GPa (Fig. 3a) and other three compounds including m-C_2NH_8, m-CNH_4 and p-CN_2H_4 (Fig. S3)[48] at high pressures were calculated and the results reveal that they are nonmetallic. In all cases, the DOS below the Fermi level mainly consist of the C-sp, N-sp, as well as the H-s orbitals, indicating the strong C–N, N–N, C–H, and N–H bonds.

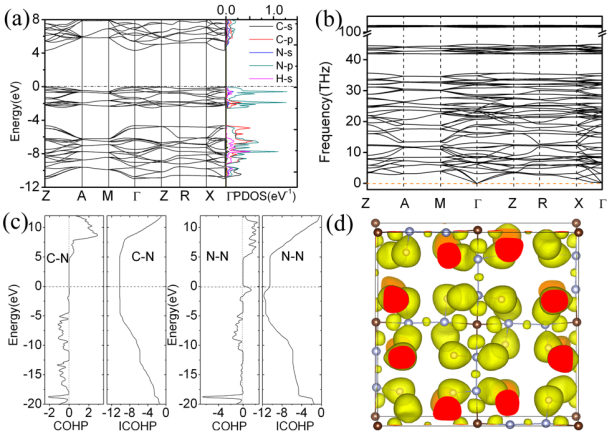

Figure 3 Electronic properties and phonon dispersion curve of I-42d phase for p-CN_4H_4 at 0 GPa. (a) Electronic band structure and density of states. (b) phonon spectrum. (c) Calculated Crystalline Orbital Hamiltonian Population and Integrated Crystalline Orbital Hamiltonian Population of C-C and N-N pairs. The horizontal lines present the Fermi levels. (d) Three-dimensional valence electron localization functions with isosurface value of 0.85.

To probe the thermodynamical origins of the stabilization of m-C_2NH_8, m-CNH_4, p-CN_2H_4, and p-CN_4H_4, we break the reaction enthalpies ΔH into the contributions from the internal energies ΔU, and the pressure-volume term ΔPV at 50 GPa (Fig. 4a). We see that ΔU is generally positive and becomes larger with higher nitrogen composition (top panel in Fig. 4a), while the ΔPV term (middle panel in Fig. 4a) is always negative and larger with increasing Nitrogen composition. The general trend of ΔH (bottom panel in Fig. 4a) resembles that of ΔPV, indicating that the volume reduction is the major driving force of these reaction. This is due to the fact that the methane-nitrogen compounds are densely packed since they form polymeric C-N and N-N covalent network (see Fig. 2).

We note that once temperature effects are included via quasi-harmonic free-energy calculations[47], the stability range of the discovered methane nitrogen compounds all shift toward higher pressure with increasing temperature (Fig. 4b).

At ambient pressure, the metastable three-dimensional covalent I-42d phase is expected to decompose exothermically to the products as solid methane and nitrogen.

$$CN_4H_4 \rightarrow CH_4 + 2N_2 + 4.8\ \text{eV}$$

The chemical energy released during this reaction is estimated to be 4.8 eV per CN_4H_4 unit at the PBE level, which corresponds to volume or mass energy densities of approximately 11.98 kJ·cm^{-3} or 6.43 kJ·g^{-1}, which is the highest energy density among the known polynitrogen compounds (Fig. 4c). Such a high energy density will place p-CN_4H_4 as a more favorable HEDM comparing with the conventional explosives such as TATB, RDX, and HMX, which typically have the energy densities ranging from 1 to 5 kJ·g^{-1} [52]. Amazingly, the weight ratio (w.t.) of nitrogen in CN_4H_4 is as high as 80%.

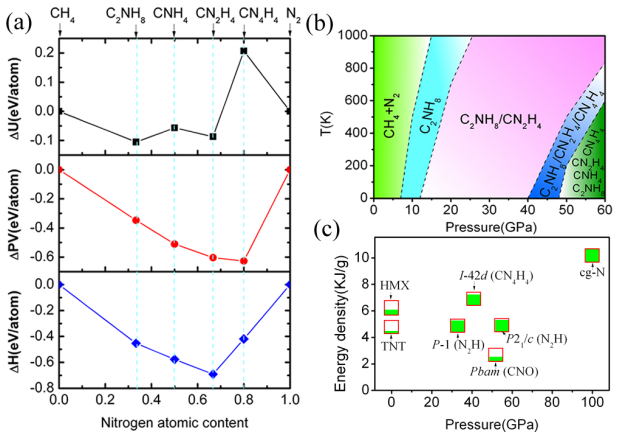

Figure 4 Formation mechanism, phase diagram and energy densities of CH_4-N_2 compounds. (a) Internal energies (top panel), PV energy terms (middle panel), and formation enthalpies (bottom panel) for CH_4-N_2 compounds relative to CH_4 + N_2 at 50 GPa. (b) Temperature versus pressure phase diagram of CH_4-N_2 system. Dashed lines show the proposed phase boundaries. (c) Calculated energy densities of the polymeric CN_4H_4 phase at ambient pressure in relation to the pressure required to stabilize them. The green scale represents the w.t. of nitrogen.

In summary, based on swarm-intelligence structure searches and first principles calculations, we predicted four new stable methane-nitrogen compounds under high pressure, including amine m-C_2NH_8, diamine m-CNH_4, and polymeric compounds of p-CN_2H_4 and p-CN_4H_4. ELF calculations reveal that the coordination numbers of C and N in all these compounds are 4 and 3, respectively. m-C_2NH_8 can be thermodynamically stable at a relatively low pressure (below 8 GPa), and one-dimensional frameworks of $Pca2_1$ phase for p-CN_2H_4 becomes stable

above 11 GPa. Three-dimensional framework *I*-42*d* phase of *p*-CN_4H_4 is predicted to be thermodynamically stable above 41 GPa that is lower than the required pressure for stabilizing cg-N, suggesting that it may be prepared more easily by high pressure synthesis. Strikingly, *p*-CN_4H_4, which is recoverable at ambient pressure, can release an enormous amount of energy (6.43 $kJ \cdot g^{-1}$) while decomposing to molecular nitrogen and methane, making it a promising new HEDM compared to conventional explosives.

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